AD-273 717

DETECTION OF VEHICLE EXHAUST/ PETROLEUM VAPORS

Margaret Schafer

Franklin Institute Research Laboratories

Prepared for:

Army Land Warfare Laboratory

March 1971

DISTRIBUTED BY:



National Technical Information Service U. S. DEPARTMENT OF COMMERCE 5285 Port Royal Road, Epringfield Va. 22151 TECHNICAL REPORT NO. LML-CR-05PA70

DETECTION OF VEHICLE EXHAUST/PETROLEUM VAPORS

by

Margaret Schafer
Franklin Institute Research Laboratories
Benjamin Franklin Parkway
Philadelphia, Pennsylvania 19103

March 1971

Final Report
Contract No. DAADO5-68-C-0283

APPROVED FOR PUBLIC PELEASE; DISTRIBUTION UNLIMITED

U.S. ARMY LAND WARFARE LABORATORY

Aberdeen Proving Ground, Maryland 21005

Reproduced From Best Available Copy

T. B.

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

| REPORT DOCUMENTATION PAGE  | REAL INSTRUCTIONS BEFORE COMPLETING FORM   |
|--|--|
| REPORT NUMBER 2. GOVT ACCESSI  | ION NO. 3. RECIPIENT'S CATALOG NUMBER  |
| LWL-CR-05PA70  |  |
| . YITLE (and Subtitie)   | 5. TYPE OF REPORT & PERIOD COVERED   |
| Detection of Vehicle Exhaust/Petroleum   |  |
| Vapors   | Final  |
|  | 6. PERFORMING ORG. REPORT NUMBER   |
| 7. AUTHOR(e)   | F-C2200-32   |
| Margaret Schafer   | Contract No.   |
| nat garas senater  | DAAD05-68-C-0283   |
|  |  |
| PERFORMING ORGANIZATION MAME AND ADDRESS   | 10. PROGRAM ELEMENT, PROJECT, TASK<br>AREA & WORK UNIT NUMBERS   |
| Franklin Institute Research Laboratories   |  |
| Benjamin Franklin Parkway  | LWL Task No. 05-PA-70  |
| Philadelphia, PA 19103  1. CONTROLLING OFFICE NAME AND ADDRESS   | 112 000007 0475  |
|  | 12. REPORT DATE  |
| US Army Land Warfare Laboratory  | March 1971   |
| Aberdeen Proving Gound, MD 21005   | 32   |
| 14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling C   |  |
|  |  |
|  | Unclassified   |
|  | 150. DECLASSIFICATION/DOWNGRADING  |
| 6. DISTRIBUTION STATEMENT (of this Repost)  Approved for public release; distribution un   | limited.   |
|  |  |
| Approved for public release; distribution un   |  |
| Approved for public release; distribution un   |  |
| Approved for public release; distribution un   |  |
| Approved for public release; distribution un   |  |
| Approved for public release; distribution un   | erent from Rapori)   |
| Approved for public release; distribution un   | erent from Rapoti)   |
| Approved for public release; distribution un   | erent from Rapoti)   |
| Approved for public release; distribution un  7. DISTRIBUTION STATEMENT (of the abeliact entered in Block 20, 11 diff.  18. SUPPLEMENTARY NOTES  9. KEY WORDS (Continue on reverse side if necessary and identify by block petroleum vapors detecti  | erent from Rapoti)   |
| Approved for public release; distribution un  The Distribution Statement (of the abeliact entered in Block 20, II different supplementary notes  Supplementary notes  Rey words (Continue on reverse side if necessary and identify by block petroleum vapors detectifuel vapors commerce  | number) Interpretation (in the following struments that equipment)   |
| Approved for public release; distribution un  7. DISTRIBUTION STATEMENT (of the abetract entered in Block 20, If diff.  18. SUPPLEMENTARY NOTES  9. KEY WORDS (Continue on reverse side if necessary and identify by block petroleum vapors detectifuel vapors commerce hydrocarbons pollutions  | number)  |
| Approved for public release; distribution un  7. DISTRIBUTION STATEMENT (of the abetract entered in Block 20, If diff  18. SUPPLEMENTARY NOTES  9. KEY WORDS (Continue on reverse side if necessary and identify by block petroleum vapors detectified vapors commerce hydrocarbons pollution inorganic pollutants   | number)  In instruments cial equipment on monitors   |
| Approved for public release; distribution un  7. DISTRIBUTION STATEMENT (of the abetract entered in Block 20, II diff.  8. SUPPLEMENTARY NOTES  9. KEY WORDS (Continue on reverse side if necessary and identify by block petroleum vapors detectifuel vapors commercially by distributions inorganic pollutants  9. ABSTRACT (Continue on reverse side if necessary and identify by block in organic pollutants   | number)  on instruments cial equipment ion monitors  |
| Approved for public release; distribution un  7. DISTRIBUTION STATEMENT (of the abetract entered in Block 20, II diff.  8. SUPPLEMENTARY NOTES  9. KEY WORDS (Continue on reverse side if necessary and identify by block petroleum vapors detectifuel vapors commercing hydrocarbons pollutants  9. ABSTRACT (Continue on reverse side if necessary and identify by block this report describes the results of a literal  | number)  on instruments cial equipment ion monitors  number) ature search and investigation to   |
| Approved for public release; distribution units of a literate determine (a) the statement of the shallowers and identify by block petroleum vapors fuel vapors commerce hydrocarbons inorganic pollutants  O. ABSTRACT (Continue on reverse side if necessary and identify by block determine (a) the trace quantities of vehicle  | number)  on instruments cial equipment ion monitors  number) ature search and investigation to e exhaust products (including fuel  |
| Approved for public release; distribution units approved for public release; distribution units approved for public release; distribution units approved for the abetract entered in Block 20, It differs to the suppression of the suppression o | number) ion instruments cial equipment ion monitors number) ature search and investigation to e exhaust products (including fuel nicles and (b) hydrocarbon and  |
| Approved for public release; distribution un  The distribution statement (of the abeliact entered in Block 20, If different entered in Block 20, If differed in Block 20, If different entered in Block 20, If different entered in Block 20, If different entered in Block 20, If differed in Block 20, If different entered in Block 20, If different en | number) ion instruments cial equipment ion monitors  number) ature search and investigation to e exhaust products (including fuel iicles and (b) hydrocarbon and y source. The object of the study the quantities present, technique |
| Approved for public release; distribution un  The distribution statement (of the abetract entered in Block 20, If diff.  This report describes the results of a litera determine (a) the trace quantities of vehicle additives) present in the atmosphere due to any petroleum vapors in the atmosphere due to any   | number) ion instruments cial equipment ion monitors  number) ature search and investigation to e exhaust products (including fuel iicles and (b) hydrocarbon and y source. The object of the study the quantities present, technique |

## FOREWORD

The work described in this report was performed under a work assignment (number 32) of Contract No. DAADO5-68-C-0283. The Franklin Institute Research Laboratories wishes to acknowledge the technical assistance given by Mr. C. McDowell of The Applied Physics Branch, U.S. Army Land Warfare Laboratory.

The principle engineer on the project at FIRL was Dr. M. Schafer, Senior Research Scientist, Chemistry Depa tment. Other FIRL contributors included W. Collins, Manager of the Mulcidisciplinary Projects Laboratory, S. Huston of the Systems Science Department and B. Epstein of Science Information Services.

Preceding page blank

# **ABSTRACT**

This report describes the results of a literature search and investigation to determine (a) the trace quantities of vehicle exhaust products (including fuel additives) present in the atmosphere near vehicles and (b) hydrocarbon and petroleum vapors in the atmosphere due to any source. The object of the study was to determine specific compounds present, the quantities present, techniques for detecting these trace compounds and equipment presently commercially available for this purpose.

# TABLE OF CONTENTS

THE COMPANY OF THE PROPERTY OF

|    |       |                                       | Page        |
|----|-------|---------------------------------------|-------------|
|    | FOREW | ORD                                   | v           |
|    | ABSTR | ACT                                   | γi          |
| 1. | INTRO | DUCTION                               | 1           |
| 2. | SOURC | ES                                    | 2           |
| 3. | LABOR | ATORY TECHNIQUES                      | 4           |
|    | 3.1.  | Total Analysis for Organic Substances | 4           |
|    |       | 3.1.1. Mass Spectrometry              | 4<br>5<br>6 |
|    | 3.2.  | Analysis of Hydrocarbons              | 6           |
|    | 3.3.  | Paraffinic Hydrocarbons               | 6           |
|    | 3.4.  | Acetylene and Acetylenic Hydrocarbons | 7           |
|    | 3.5.  | Olefinic Hydrocarbons                 | 8           |
|    | 3.6.  | Aromatic Hydrocarbons                 | 9           |
|    | 3.7.  | Oxygenated Compounds                  | 9           |
| 4. | INORG | ANIC GASEOUS POLLUTANTS               | 10          |
|    | 4.1.  | Sulfur Dioxide                        | 10          |
|    | 4.2.  | Nitrogen Dioxide                      | 11          |
|    | 4.3.  | Carbon Monoxide                       | 11          |
| 5. | CONCL | USIONS                                | 12          |
|    | APPEN | DIX A                                 | A-1         |
|    | ADDEN |                                       | D 1         |

# 1. INTRODUCTION

This report contains information obtained from the literature on the possible pollutants emitted from military targets and the currently available methods of detection. This search is by no means exhaustive, but was conducted within the level of effort of the program. As much as possible of the trade literature on monitors has been covered. However, there are undoubtedly some instruments we may have missed.

The use of air pollutant monitors to spot military targets is very definitely feasible within the limits of current technology. If the exact type of target were defined as well as the monitoring conditions, we could make specific recommendations.

## 2. SOURCES

For both stationary and mobile sources the concentration of pollutants emitted depends on the combustion conditions. In industrialized countries where there are emission control standards the emissions will be different than in countries where there are no restrictions. Appendix A gives the concentrations of pollutants emitted from sources under various conditions. The types of pollutants emitted by each source are summarized in Table 1.

It should also be considered that these pollutants undergo a large variety of photochemical reaction. Consequently the types of compounds present as well as the concentrations will vary over a period of time.

Table 1 POLLUTANT

| NO <sub>2</sub> SO <sub>2</sub> CO Aldehydes Hydrocarbon Paraffins Olefins | *                            | * *  | *            | *          | *            | * *                 |  |
|--|------------------------------|--|--------------|------------|--------------|---------------------|--|
| Source   | Natural Gas Fired Appliances | Natural Gas Fired Industrial<br>& Commercial Equipment | Auto Exhaust | → Aircraft | Diesel Motor | 011-Fired Equipment |  |

#### 3. LABORATORY TECHNIQUES

Many laboratory instrumental techniques have been applied to the analysis of air pollutants. All of this type of instrumentation is available commercially. However, as they are produced for laboratory analysis they are usually too large and cumbersome, and also more versatile than necessary, for a portable or semi-portable pollutant monitor. All of this type of instrumentation can be modified for a particular set of sampling conditions and many companies are producing monitors which are based on laboratory instrumentation. These monitors are mostly produced for non-military applications whose conditions are not the same as those used for spotting military targets. Consequently, we are including this discussion of laboratory-type instrumentation, because after the type of target and monitoring conditions are defined it may be easier to streamline laboratory equipment to do the analysis rather than to try to use a civilian type of monitor. The sampling requirements may be quite different in the two cases. Especially if the monitor is required to be in an airplane or helicopter.

## 3.1. Total Analysis for Organic Substances

Mass spectrometry, dispersive and non-dispersive infrared instrumentation and flame ionization analyses have been applied to the analysis for total organic substances. However, since different organic substances respond differently to the different measurement techniques, care is needed in interpreting and comparing any data.

## 3.1.1. Mass Spectrometry

Mass spectrometry has been applied to total organic substance analysis and fairly good agreement was obtained among the investigators. In these measurements the samples were collected by freezing and then

injected into the mass spectrometer. However, a diaphragm which allowed only the pollutant to diffuse through could also be used. The problem with using mass spectrometry to measure mixtures of pollutants is that the data is very difficult to interpret. The sample is ionized in the mass spectrometer so that it acquires a charge and is fragmented. Then the mass of the fragments is determined by their deflection in a magnetic field. Each compound has a characteristic fragmentation or cracking pattern which can be used for identification. However, when mixture of pollutants is introduced, their cracking patterns are superimposed and relative reak heights depend not only on the compounds present but also on the relative amounts. For this type of analysis a computer is often attached to the mass spectrometer so that the pattern can be compared electronically to those of known mixtures.

Another means of simplification is possible. The mixture can be fed first through a gas chromatograph which will separate most of the components of the mixture. Each component will then be fed into the mass spectrometer for identification.

## 3.1.2. Infrared Techniques

Both dispersive and non-dispersive infrared techniques have been used to measure total hydrocarbons. In many of these cases oxygenated compounds were removed chemically and then the 3.45  $\mu$  band was used to estimate total hydrocarbon. This is often referred to as ppm n-hexane. The widespread use of non-dispersive infrared measurements and the comparison to n-hexane comes from its being accepted as a standard in California. Since methane and unsaturated hydrocarbons give a reduced response at 3.45  $\mu$  after their concentrations are measured by using another infrared frequency. Although most of these analyzers are designed with complicated optics and long path length cells, the characteristic infrared absorption and emission spectra of organic substances are well suited to remote monitoring techniques.

#### 3.1.3 Flame Ionization Aralyzers

The flame ionization analyzer for total hydrocarbons is similar to the flame ionization detector for gas chromatography. Its response is fairly proportional to the number of carbon atoms in the molecule and is unresponsive to inorganic materials. It has been widely used for monitoring total hydrocarbons, particularly from automobile emissions. Its only drawback is that large molecules tend to be adsorbed on the walls before they reach the detector.

# 3.2. Analysis of Hydrocarbons

Mass spectrometry and infrared spectrometry are difficult to use for measuring trace quantities of particular hydrocarbon in a polluted atmosphere. Both of these techniques require concentration of the sample before it can be measured. Gas chromatography allows the analysis of particular hydrocarbons without concentration of the sample. In gas chromatography the sample passes through a column packed with a solid or a liquid suspended on a solid. The length of time a particular hydrocarbon takes to pass through the column depends on how strongly it interacts with the substrate. Thus with the proper choice of column packing material a sample containing a mixture of materials will emerge as a series of peaks each containing one material. There are several types of detectors used with gas chromatographs; the common ones are flame ionization and thermal conductivity. For hydrocarbons flame ionization is the most gensitive

# 3.3, Paraffinic Hydrocarbons

Mass spectrometry, infrared spectrophotometry and gas chromatography have been used. There are also techniques available to remove all hydrocarbons except paraffinic hydrocarbons so that a flame ionization analyzer can be used.

Analysis of particular paraffinic hydrocarbons by mass spectrometer is difficult, because of the low intensity of the high mass peaks and interference from other hydrocarbons. Usually methane is determined from the m/e peak of 15 and higher paraffins are determined as a group. A mercuric perchloride tube can be used to remove olefins and oxygenated compounds in order to simplify the mass spec analysis. Mass spec has been used successfully in areas such as petroleum refineries where paraffin concentrations are high.

Infrared spectrophotometry has not proved useful for the analysis of pararfinic hydrocarbons. Methane can be analyzed by its absorption peak at 7.6  $\mu$ , but analysis of other paraffins is not practical. Although the peak at 3.4  $\mu$  is largely a paraffin absorption, there is too much interference from paraffin groups on other hydrocarbons.

Gas chromatography is the best way for analyzing mixtures for paraffinic hydrocarbons. Various substrates such as silica gel can be used to separate paraffinic hydrocarbons up to the hexanes. Chromatographic techniques for separating higher molecular weight hydrocarbons such as in diesel fuel have also been developed. Sometimes two columns are combined; one to remove unsaturated hydrocarbons and the second to separate the paraffins.

#### 3.4. Acetylene and Acetylenic Hydrocarbons

The use of mass spectrometry for analysis of acetylene in air is limited by sensitivity because the concentrations are around 0.2 ppm. However, it has been used with minor corrections for analysis of acetylene in automobile emission where the concentrations are higher. Analysis of higher molecular weight acetylenic compounds are interfered with by diolefins and cycloolefins.

Infrared spectrometry can be used to identify acetylene by its absorption band at 13.7  $\mu$ . Corrections for carbon dioxide are necessary.

Gas chromatography can be used to analyze and separate acetylene from most types of samples. Various substrates such as silica gel, 20 m Carbowax on alumina and dimethylsulfolane on firebrick can be used. Higher molecular weight acetylenic compounds have also been separated by gas chromatography.

# 3.5. Olefinic Hyd: warbons

Many types of procedures have been developed for determining olefins in emissions and polluted atmospheres, these include: spectrophotometric, coulometric, mass spectrometric, infrared and gas chromatographic.

Several methods involving the bromination of olefins have been used. An instrument based on a "bromocoulometric" system has been developed. The bromination is carried out before coulometry, and the amount of olefin is proportional to the time needed to generate the bromine absorbed by the sample. This technique is interfered with by inorganic pollutants such as sulfur dioxide and nitrogen dioxide.

Mass spectrometry gives an incomplete analysis of olefins. Only a few can be identified by this technique, the rest encounter difficulties with overlap and sensitivity.

Infrared spectroscopy has been useful in identifying certain olefins. However, in most cases a long pathlength is necessary.

Gas chromatography has proven to be a very powerful tool for the analysis of olefins. It is possible to separate olefins up to the pentenes on substrates such  $\sim 20$  m Carbowax,  $\beta$ ,  $\beta$  oxidipropionitrile on alumina or dibutylmaleat. Bigher molecular weight hydrocarbons can be analyzed by

temperature programming the column. Diolefins react with nitrogen dioxide so automobile exhaust samples must be diluted if they have to be stored for long periods of time before analysis.

#### 3.6. Aromatic Hydrocarbons

Mass spectrometry has been used to identify benzene, toluene, xylenes and styrene in emissions and polluted atmospheres. Also total aromatics have been determined.

Infrared methods have not been extensively used.

Gas chromatography can be used to separate and identify aromatic hydrocarbons. Aromatic hydrocarbons in the six to eleven carbon atom range can be separated on a Carbowax 1540 column and identified with flame ionization detector. By the use of temperature programming it is possible to analyze both aliphatic and aromatic hydrocarbons on the same column.

# 3.7. Oxygenated Compounds

Instrumental analytical techniques have not proved useful for the analysis of oxygenited compounds. Most analyses are done with wet chemical or colorimetric techniques. Although infrared spectroscopy, mass spectrometry and gas chromatography have been tried, they have not developed into useful techniques.

## 4. INORGANIC GASEOUS POLLUTANTS

# 4.1, Sulfur Dioxide

The most commonly used methods for sulfur dioxide analysis are conductimetric, titrimetric, colorimetric, turbidimetric and iodimetric. These methods can be carried out manually or incorporated into monitoring instruments.

The West-Gaeke Method (colorimetric) is applicable to the determination of sulfur dioxide in the concentration range 0.005 to 5 ppm. The sulfur dioxide is absorbed in 0.1 m sodium tetrachloromercurate and the dichlorosulfitomercuric ion is formed. The addition of acid-bleached pararosaniline and formaldehyde to the complexion produces red-purple pararosaniling methylsulfonic acid which is determined spectrophotometrically.

Hydrogen Peroxide Method (titrimetric) is applicable to the determination of  $SO_2$  in the concentration range 0.01 to 10.0 ppm.  $SO_2$  is absorbed in 0.03 N hydrogen peroxide reagent (adjusted to about pH 5). The sulfuric acid formed is titrated with standard alkali.

The conductivity method can be applied to sulfur dioxide in the concentration range of 0.01 to 2 ppm. The sulfur dioxide is absorbed in a slightly acidic hydrogen peroxide solution. The change in conductivity of the solution is monitored. This method is interfered with by any gas which forms a strong electrolyte in solution.

Indimetric method has been used to monitor sulfur dioxide concentrations. A set of standards is prepared by measuring the optical absorption of dilute starch-iodine solutions containing various amounts of sulfuric acid. This is compared with the absorption of a starch-iodine solution in which the sulfur dioxide from the atmospheric sample has been absorbed.

Barium Sulfate method (turbidimetric) uses a dilute hydrogen peroxide solution to absorb the sulfur dioxide. It is then precipitated as barium sulfate and the suspension stabilized by glycerol-alcohol. The turbidity of the solution is measured with a spectrophotometer.

Sulfur dioxide can be measured also on a special gas chromatograph with a flame photometric detector.

# 4.2. Nitrogen Dioxide

The Saltzman method is sensitive to nitrogen dioxide over a range of a few parts per billion to about 5 ppm. This method is based on the Guiess-Ilosvay reaction in which a pink-cloud dye complex is formed between sulfanilic acid, nitrite ion, and  $\alpha$ -naphthylamine in an acid medium. The color is measured photometrically.

Nitrogen oxide can also be measured on a special gas chromatograph with a flame photometric detector.

#### 4.3. Carbon Monoxide

Various colorimetric methods as well as gas chromatography and infrared spectroscopy have been used to measure carbon monoxide.

The gas chromatographic technique used to measure carbon monoxide employs a flame ionization detector and a double column. The sample goes through a column packed with di-2-ethyl-hexyl sebacate on 60-80 mesh "columnpak" and then a column packed with 42-60 mesh molecular sieves to separate the carbon monoxide. The carbon monoxide is then catalytically reduced with hydrogen to methane with a catalyst such as nickel powder and the methane is measured quantitatively with the flame ionization detector.

The infrared absorption of carbon monoxide has been utilized in the construction of several non-dispersive infrared spectrometers. These have pressurized longpath length cells in addition to the usual source, detector, chopper and amplifiers in as usual infrared spectrophotometer.

## 5. CONCLUSIONS

Table II gives a summary of the laboratory methods best applicable for the analysis of various pollutants. In Table III is given the commercial air pollutant monitors and the pollutants they detect. These monitors are described in Appendix B. Since these descriptions were obtained from sales literature in which the units are described as magic boxes, some of the techniques are not too clear.

There are two new techniques which should be mentioned. One is the use of the microwave spectra for the development of instrumentation. This is currently thought highly of by NAPCA (private communication R. Stevens). The second is the Pyrochrom Analyzer which although it has not been applied to air pollution studies has been used successfully for other analytical applications. This system could easily be converted to a monitor for a particular pollutant (private communication Eugene Levy - Control Data Systems.

TABLE II
ANALYTICAL TECHNIQUE

| Pollutant                  | Wet<br><u>Chemical</u> | Mass<br>Spectrograph | Infrared   | Gas<br><u>Chromatograph</u> | Flame<br>Ionization |
|----------------------------|------------------------|----------------------|------------|-----------------------------|---------------------|
| Total<br>Organic           |                        | *                    | <b>5</b> % |                             | *                   |
| Paraffins                  |                        | *                    | *          | **                          |                     |
| Acetylenic<br>Hydrocarbons |                        | *                    | *          | **                          |                     |
| Olefins                    | ;\                     | *                    | 5/5        | **                          |                     |
| Aromatics                  | *                      |                      |            | **                          |                     |
| Oxygenated<br>Hydrocarbons | *                      |                      |            |                             |                     |
| so <sub>1</sub>            | *                      |                      |            |                             |                     |
| NO <sub>2</sub>            | *                      |                      |            |                             |                     |
| CO                         | *                      |                      | *          | <u></u>                     |                     |

Legend \*\* Best Method

TABLE III
POLLUTANT

| Commercial Unit                   | <u>co</u>  | <u>so<sub>2</sub></u> | NO <sub>2</sub> | Hydrocarbon |
|-----------------------------------|------------|-----------------------|-----------------|-------------|
| Intertech System                  | , <u>,</u> | *                     | *               |             |
| Beckman Hydrocarbon<br>Analyser   |            |                       | ×               |             |
| Beckman IR                        | *          | *                     |                 | *           |
| Beckman Ultraviolet<br>Photometer |            |                       | *               |             |
| Combust Gas Detect                |            |                       |                 | *           |
| Portable Gas<br>Chromatograph     | *          |                       |                 | *           |
| Melpar                            |            | *                     |                 |             |
| Dynasciences                      |            | *                     | *               |             |

APPENDIX A

Δ

gf -\_\_\_\_\_\_\_\_

|  | $\frac{d}{dt}$ Nitrogen Oxides $\frac{d}{dt}$ as $(NO_2)$ | च Aldehydes                              | d Ammonia | ad Acids | Z OS mppm | امد Carbon Monoxide                                  | Reference   |
|--|---|--|-----------|----------|-----------|--|---|
| Natural Gas<br>Fired<br>Appliances   |   |  |           |          |           |  |   |
| Bunsen Burner Range, top burner Range, oven Water Heater, 20 gal. Water Heater, 100 gal Floor Furnace Forced Air Furnace Steamboiler Low fire High fire Industrial Burners Natural Gas Fired Industrial and Commercial Equipment | 21<br>22<br>15<br>25<br>45<br>30<br>50<br>40<br>90<br>216 | 2<br>11<br><br>8<br>3<br><br>5<br><br>49 | 0.5       | 30       | 4         |  | (1)<br>(1)<br>(1)<br>(1)<br>(1)<br>(1)<br>(1)<br>(1)<br>(2) |
|  |   | Typlo                                    | al Ran    | ges      |           |  |   |
| Scotch Marine Boilers Fire Tube Boilers Water Tube Boilers 75 gal Water Heaters Space Heater Bake Oven Industrial Ovens, Indirect Ceramic Kilns,   | 8-56<br>35-34<br>16-127<br>46<br>19<br>20                 | 2-7<br>4<br>3-11<br>2<br>2<br>6          |           |          | •         | 0.0-0.2<br>0.0-0.1<br>0.0-0.2<br>0.001<br>0.0<br>0.0 | (3)<br>(3)<br>(3)<br>(3)<br>(3)<br>(3)                      |
| Indirect   | 3-66  | 2-7                                      |           |          |           | 0.00-0.04  | (3)   |

| %sebixo negonil∥                                 | 0.38-0.95            | 2.5     | 77 0     | 0.00      |             |       | 0.30                | 0.36        | 0.11       | (5)              |
|--|----------------------|---------|----------|-----------|-------------|-------|---------------------|-------------|------------|------------------|
| Formaldehyde*                                    | 0.1-0.25             | 0.17    | 90       | 00.0      |             | 0.14  | 160-1100 0.21-0.38  |             |            | (†)              |
| farbon monoxide**                                | 5-44                 | 1       | o.       | 67        |             |       |                     |             | 3500       | (†)              |
| Single atom<br>hydrocarbon**                     | 1-10                 | !       |          |           |             | ~     | 36-120              |             | 730        | (†)              |
| Benz (a) anthracene                              |                      |         |          |           |             |       | 8.6                 | 1.23        |            | ( <del>*</del>   |
| Fluoranthene*                                    |                      | 0.17    | 2        | 0.79      | :           | .50   | 83.9                | 7.1         | 2,200      | ( <del>*</del>   |
| *enanthrene*                                     |                      |         |          |           |             |       | 22                  | 2.2<br>64   | 2,200      | (†)              |
| *eneseatd1nA                                     |                      |         |          |           |             |       | <u>.</u>            |             | 989        | (†)              |
| *ənəño1oJ  | 0-0.15               | 0.01    | ć        | 0.057     |             |       | 0.73                | 2.64        | 99         | (†)              |
| *anaserd1nA                                      | 0-0.02               |         |          |           |             |       | 0.64                |             | 198        | ( <del>†</del> ) |
| <br> Benzo(ghi)perylene*                         | 0.02                 | 0.44    |          |           |             |       | 9.9<br>9.9          | 1.28        | 9,20       | (4)              |
| Perylene $^{x}$                                  | 0-0.15               | 0.07    |          |           |             |       | 3.5                 |             | 132        | ( <del>†</del> ) |
| Benzo (e) py rene*                               | 0-0.5                | 0.87    | 2        | 0.77      | •           | 0.29  | 17                  | 0.51        | 220        | (4)              |
| Pyrene*  | 0.2-                 | 2.25    | ,,       | 7.27      | ı           | 0.86  | 35                  | 3.7         | 1,320 220  | (4)              |
| Benzo (a) pγrene"                                | 0.04- 0.2-           | 0.49    | ĉ        | 0.057 1.3 |             | 0.082 | 22 35               | 0.26<br>8.4 | 880        | (4)              |
| Solid Fuel Various Firing Methods for Bituminous | Pulverized<br>Firing | Cyclone | Spreader | מ מאסיים  | Chain Grate |       | oderfeed<br>Stokers |             | Hand Fired | Reference        |

\*Pounds per billion Btu input.

\*\*Pounds per million Btu input.

†Units: pounds per million-million Btu input.

Industrial and Commercial Oil Fuel Equipment

|                             | Rated      | 0:1<br>9:4              | so,         | \$0s  | 03         | Aldehydes<br>(as<br>formaldehyde) | Nitrogen<br>Oxide<br>(as NO <sub>2</sub> ) | Remarks<br>011 P<br>AP | oil Properties | Ash        | Excess Ref.       |
|-----------------------------|------------|-------------------------|-------------|-------|------------|-----------------------------------|--|------------------------|----------------|------------|-------------------|
| Equipment                   | (hp)       | (ghp)                   | (mdd)       | (mdd) | (%)        | (mdd)                             | (mdd)                                      | gravity                | (%)            | (%)        | air (%) (3)       |
|                             |            |                         |             | ᆂᆝ    | Number 2   | Fuel 0il                          |  |                        |                |            |                   |
| Firetube<br>boiler          | 3 6        | 9<br>39.6               | 355         | 9.1   | 0.01       | <b>6</b> √0                       | 47<br>14                                   | 35                     | 1.05           | 1.02       | 65<br>220         |
| Scotch<br>marine<br>boilers | 200<br>350 | 21.0<br>85.3            | 17          | 5.6   | 0.02       | 52                                | 21   | 34<br>33               | 0.97           | 00         | 210<br>94         |
| Water tube<br>boiler        | 200        | 6.1                     | 98<br>trace | 4.00  | 0.002      | ₩.                                | 36<br>33<br>33                             | 29<br>35               | 0.71           | 0000       | 290<br>370<br>115 |
| 0:1 heater                  | 7 :        | - 64                    | 138         | 2.5   | 0.002      | ,                                 | 34   | ) m                    | 0.80           | 0          | 120               |
|                             |            |                         |             | Z]    | Number 1   | Fuel 0il                          |  |                        |                |            |                   |
| Scotch marine<br>boiler     |            | 15.3                    | 28          | 1.7   | 0.001      | rV (                              | 50   | 04                     | 0.09           | 0          | 150               |
| Ceramic<br>kiln             | 1 1        | 10.0<br>20.0            | 0<br>trace  | 00    | 0.04<br>0  | mm                                | 2/<br>20                                   | <b>4</b> 4 5 5         | trace          | <b>)</b> 0 | 21<br>373         |
|                             |            |                         |             | T)    | Heavy Fuel | 1 011                             |  |                        |                |            | ,                 |
| Firetube<br>boiler          | 120        | 36.3                    | 414         | 4.7   | 0.003      | 7                                 | 368  | 15                     | 0.0            | 0          | 89                |
| Scotch marine               | 125        | 23.1                    | 797         | 3.2   | 0          | δ                                 | 128  | =                      | 1.78           | 0.18       | 180               |
| Water tube                  |            | 4.66                    | 397         | 4.0   | 0          | ∞ -                               | 387  | = °                    | 0.44           | 0.13       | 43                |
| boiler                      | 425        | 20.00<br>20.00<br>20.00 | 367         |       | 20.0       | 4 L                               | 661  | ° <u>~</u>             | 2.00           | 0.12       | 107               |
|                             | 200        | 248.0                   | 594         | 3.6   | 0          | 17                                | 256  | . 5                    | 1.39           | 0.04       | 92                |
|                             | 580<br>870 | 57.5                    | 944<br>344  | 2.2   | 00         | 8 8 <del>,</del>                  | 206<br>256                                 | <u>ო</u> თ             | 1.30           | 0.03       | 95<br>73          |
|                             | , , ,      |                         | `           |       |            |                                   | ,  | •                      |                | •          | 1.                |

# DIESEL EMISSION

|   | Unburned<br>Hydrocarbon  | Formaldehyde             | X<br>OX                  | 00                          | c <sub>0</sub> 2           |                          |
|---|--------------------------|--------------------------|--------------------------|-----------------------------|----------------------------|--------------------------|
| Two-cycle engine,<br>No. 2 fuel           | ррмС                     | ррт                      | ppm                      | <del>2</del>                | ٠ <u>٠</u>                 | Reference                |
| Full Load<br>Half Load<br>No Load<br>Idle | 467<br>605<br>530<br>401 | 13<br>8.1<br>7.3         | 622<br>392<br>147<br>210 | 0.1<br>0.03<br>0.03<br>0.03 | 6.0<br>3.6<br>1.53<br>1.0  | (6)<br>(6)<br>(6)<br>(6) |
| Four-cycle engine,<br>No. 2 fuel          |                          |                          |                          |                             |                            |                          |
| Full Load<br>Half Load<br>No Load<br>Idle | 29<br>68<br>73<br>104    | 4.3<br>6.8<br>:.8<br>6.8 | 921<br>493<br>109<br>119 | 0.2<br>0.03<br>0.03<br>0.03 | 10.6<br>5.2<br>1.21<br>0.9 | (6)<br>(6)<br>(6)<br>(6) |

|                                      | Remarks and ref. | After (7) 1963 this<br>type of emission is | totally controlled in<br>U.S. made cars. |
|--------------------------------------|------------------|--|--|
| Tota! hydrocarbon                    |                  | 15060                                      | 1365                                     |
| Acetylenes                           |                  | 09   | 582                                      |
| əuəz u <b>ə</b> g                    |                  | 270  | 75                                       |
| enesnudoid zailemomA                 |                  | 6515                                       | 190                                      |
| Jefins C <sub>5</sub> and heavier    |                  | 1420                                       | 30                                       |
| µJ-2J enitol0                        |                  | 230  | 200                                      |
| Paraffins C <sub>6</sub> and heavier |                  | 4780                                       | 155                                      |
| go of to suithered                   | Edd              | 3150                                       | 130                                      |
| Mitrogen oxides                      | шdd              | trace                                      | 850                                      |
| Carbon monoxide                      | æ                | trace                                      | 3.12                                     |
|                                      |                  | blow-by                                    | exhaust                                  |

# AIRCRAFT TURBINE EMISSIONS

|             | Hydrocaruon | ×<br>ov | Aldehydes |           |
|-------------|-------------|---------|-----------|-----------|
| Engine Mode | <u>DmC</u>  | ppm     | ppm       | Reference |
| Idle        | 150         | 5       | 5         |           |
| Cruise      | 5           | 50      | 1         |           |
| Takeoff     | 2 .         | 5       | Trace     |           |

#### REFERENCE

- (1). F. E. Vandaveer and C. G. Segeler, Ind. Eng. Chem. 37, 816 (1945); 44, 1833 (1952).
- (2). Stanford Research Institute, "The Smog Problem in Los Angeles County", p. 130, Stanford Research Institute, Menlo Park, California 1954.
- (3). R. L. Chass and R. E. George, J. Air Pollution Control Assoc. 10, 34 (1960).
- (4). W. S. Smith and C. W. Gruber, U.S. Public Health Serv. Publ. 999-AP-24 (1966).
- (5). R. P. Hangebrauck, D. J. von Lehmden, and J. E. Meeker, J. Air Pollution Control Assoc. 267 (1964). S. T. Cuffe and R. W. Gerstle "Summary of Emissions from Coal-Fuel Power Plants" A. I.H.A. Houston, Texas, 1965.
- (6). R. W. Hurn and D. E. Seizinger, Proc. Am. Petrol. Inst. Sect. III 45, 127 (1965).
- (7). A. H. Rose, Jr., "A Summary Report of Vehicular Emissions and Their Control", presented to Am. Mech. Engrs., N. Y., 1966.
- (8). A. C. Stern, Air Pollution III, page 93.

APPENDIX B

# THE INTERTECH SYSTEM FOR GAS ANALYSIS

INTERTECH CORPORATION PRINCETON, NEW JERSEY

SAMPLING: By a probe designed for the sampling conditions

The Intertech System is comprised of various components, sensors, recorders, probes, etc., which can be combined to form a unit. Which components are chosen depends on the concentration of gases present and the conditions under which they are to be sampled.

Infrared Absorption - Uras 2

CO 0-25 ppm CO<sub>2</sub> 0-15 ppm

 $so_2$ 

NO

This detector is based on the infrared absorption of the pollutants. Parallel light beams pass through the sample and nitrogen and the difference in infrared energy transmitted causes a temperature differential and thus a pressure differential which is monitored as capacitance and converted to an electrical signal.

# BECKMAN HYDROCARBON ANALYZER

BECKMAN INSTRUMENTS INC. PROCESS INSTRUMENTS DIVISION FULLERTON, CALIFORNIA 92634

Monitors Hydrocarbons as methane Methane 0-1 ppm

Hydrocarbons burned in a hydrogen flame cause a large number of ions. By applying a polarizing voltage in the flame vicinity an ionizing current is established which produces a signal which can be amplified.

# BECKMAN INFRARED ANALYZERS MODEL IR-315A, IR-415A, IR-215A

BECKMAN INSTRUMENTS INC. PROCESS INSTRUMENTS DIVISION FULLERTON, CALIFORNIA 92634

#### MONITORS

 $\begin{array}{cc} \text{CO}_2 \\ \text{CO} \\ \text{C}_2\text{H}_2 & \text{ppm} \\ \text{CH}_4 \end{array}$ 

SO<sub>2</sub>

Uses infrared absorption to produce a signal. The sample gas is contained in a detector section which is separated into two parts by a diaphragm. Infrared radiation (as parallel beams) passes through two compartments, one containing the sample and the other non-absorbing gas, and falls onto the two sections of the detector. The sample gas absorbs some of the infrared radiation so that the two sides of the detector receive different amounts of infrared radiation which is absorbed causing a temperature difference and, therefore, a pressure difference. The pressure difference deflects the diaphragm separating the two sides. The incident radiation is chopped so that the diaphragm moves back and forth. This movement creates the signal which is monitired.

# ULTRAVIOLET FILTER PHOTOMETER BECKMAN MODEL 255A

BECKMAN INSTRUMENTS INC. PROCESS INSTRUMENTS DIVISION FULLERTON, CALIFORNIA 92634

MONITORS

NO<sub>2</sub> ppm

This instrument utilizes the ultraviolet absorption of NO<sub>2</sub> to produce an electrical signal. Light from a tungstem lamp is split and by chopping the beams the light passes alternately through the sample and a reference. Difference in intensities at the photomultiplier produces a signal which is amplified.

# COMBUSTIBLE GAS DETECTOR MODEL 179

GENERAL MOTORS INC. 3019 ENTERPRISE STREET COSTA MESA, CALIFORNIA 92626

Hydrogen 0-100% lower explosive limit Hydrocarbons

Unit consists of control unit and remote sensing probe.

Gas diffuses into the sensing probe and is oxidized at the catalytic surface causing a temperature rise which produces an electrical signal. Unit can be battery operated.

# PORTABLE GAS CHROMATOGRAPH SERIES 500

ANALYTICAL INSTRUMENT DEVELOPMENT INC. 250 S. FRANKLIN STREET WEST CHESTER, PENNSYLVANIA 19380

SAMPLING: By injection

Portable laboratory gas chromatograph. Contains rechargeable batteries and gas supply so that it can operate up to eight hours as a portable unit. Equipped with flame ionization, thermal conductivity and electron capture detectors.

## AIR POLLUTION SULFUR ANALYZER

MELPAR INC. 6631 IRON PLACE SPRINGFIELD, VTPGINIA 22150

#### MONITORS

SO<sub>2</sub> 0.01 ppm to 10 ppm H<sub>2</sub>S SO<sub>3</sub> Mercaptans Total Sulfur

SAMPLING: Air is drawn into the analyzer by the sampling pump

The analyzer is comprised of four subsystems. A Melpar Flame Photometric Detector (FPD), patent pending, a Photometer, a Gas Flow System, and Power supplies. It requires a hydrogen gas supply and 120 volt 60 Hz, 200 watts electrical power for normal operation.

The Melpar Flame Photometric Detector (FPD) utilizes the photometric detection of the 394 mp-centered band emitted by sulfur containing compounds in a hydrogen-rich/air flame. Its specificity arise the employment of a harrow band-pass interference filter and a get rangement that optically shields the photomultiplier tube from mary flame.

DYNASCIENCES AIR POLLUTION MONITORING 9601 CANOGA AVENUE CHATSWORTH, CALIFORNIA 91311

## MONITORS

 $NO_X$  5 ppm - 1500 ppm  $NO_2$  SO2 2 ppm - 5000 ppm

This monitor uses a unique electrochemical technique which allows the entire analytical process to be accomplished in a small totally enclosed and sealed transducer. Transducer converts the pollutant concentration to a current signal. Sample is drawn into the sampling conditioning unit by a pump and then into contact with the transducer.